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# PATENT SPECIFICATION

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## (54) IMPROVEMENTS IN OR RELATING TO BRAZING ALUMINIUM

- (71) We, ALCAN RESEARCH AND DEVELOPMENT LIMITED, a Company incorporated under the laws of Canada, of 1, Place Ville Marie, Montreal, Quebec, Canada, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to methods of joining aluminium (including aluminium alloys) by brazing.
- It is already known to join aluminium components by melting an aluminium brazing alloy between or adjacent the faying surfaces (i.e. the surfaces to be joined, in the presence of a flux, which dissolves or disrupts the aluminium oxide film on the metal surfaces. It is commonly preferred that the melting point of the brazing alloy be at least 30° to 40°C lower than that of the metal of the components. An example of a suitable brazing alloy is an Al-Si eutectic composition, which melts at about 577°C and thus melts at a temperature which is at least 30°C below the melting point of aluminium and most commonly used aluminium alloys.
- Although it is normal practice for at least one component to be made from brazing sheet (aluminium alloy clad with aluminium brazing alloy), it is also known to apply the brazing alloy as a powder, carried in a suitable liquid or paste-like vehicle.
- Fluxless aluminium brazing is known which requires to be performed at sub-atmospheric pressure and is therefore expensive and inconvenient. Other fluxless methods, which require the use of an inert atmosphere at atmospheric pressure, are also known, but these are highly sensitive to even trace amounts of oxygen and water vapour contamination of the atmosphere and are likewise expensive and inconvenient to operate. It is, therefore, normal practice to employ a flux in brazing aluminium to remove the oxide film ordinarily present on aluminium surfaces. The material used as a flux must be capable of dissolving or disrupting aluminium oxide at the brazing temperatures while remaining inert with respect to aluminium at such temperatures.
- It has been usual to employ mixtures of metal chlorides as fluxes for brazing aluminium. These fluxes are water-soluble and usually hygroscopic and are corrosive to aluminium (including aluminium brazing alloys) in the presence of water; hence residues of such fluxes must be removed by washing at the end of the brazing operation.
- It has already been proposed to use a mixture of a powdered brazing alloy with chloride flux in a suitable liquid vehicle. The required vehicle has thus been limited to organic liquids in which the chloride-containing flux does not attack the brazing alloy particles. Because the fluxes are hygroscopic, this expedient has not been satisfactory, since it has been necessary to proceed with the brazing operation as soon as the vehicle had dried.
- We have already described in Patent No 1,438,955 aluminium brazing fluxed consisting of one or more potassium fluoaluminate complexes (either  $KAlF_6$  alone or in admixture with  $K_2AlF_6$ ) and essentially free of unreacted potassium fluoride. These fluxes are non-hygroscopic and leave no water-soluble residue. Such fluxes are reactive at temperatures above 560°C to strip from or dissolve oxides on aluminium surfaces but are essentially inert with respect to metallic aluminium so that there is no necessity to wash a brazed assembly to remove flux residue for avoiding corrosion.
- The present invention provides a method of joining aluminium components by means of an aluminium brazing alloy having a melting point lower than that of the aluminium components, in which the assembled components are heated to a temperature above the melting point of the brazing alloy and below the melting point of

5 said components in the presence of a  
potassium fluoaluminate flux, which is  
essentially free of unreacted KF  
characterised in that the flux and the  
brazing alloy are applied to the surface of at  
least one of the components as an aqueous  
slurry of finely divided flux and metal  
powder, the film of slurry is then dried and  
the components are brazed (after assembly,  
if necessary) by heating in a dry, oxygen-  
free inert gas atmosphere, the application  
of flux/brazing alloy slurry being controlled  
to apply 30—180 gms/m<sup>2</sup> of solids and the  
flux: brazing alloy ratio being selected to  
deposit at least 3.29 gms/m<sup>2</sup> of flux.

10 We have now discovered that the said  
flux, consisting essentially of potassium  
fluoaluminate, possibly with some  
unreacted AlF<sub>3</sub>, but essentially free of  
unreacted potassium fluoride, may be  
maintained in an aqueous slurry with  
powdered aluminium brazing alloys for  
extended periods of time without deleteriously  
attacking the brazing alloy particles.  
15 We have found, very surprisingly, that  
aluminium brazing alloy particles  
and flux particles may be deposited on  
aluminium from such slurry and be dried to  
form a film which has reasonable adhesion  
to the aluminium. By contrast, a slurry of  
aluminium brazing alloy particles alone  
does not form a film of adequate adhesion.  
In some circumstances as little as 2% flux in  
the total solids of the slurry is sufficient.  
20 More usually it is preferred that the flux  
should be present in an amount of 10—20%  
of the amount of the brazing alloy particles  
by weight. The weight of water in which the  
mixture of flux and metal powder is  
dispersed may be varied depending on the  
desired consistency of the dispersion, but is  
typically less than the weight of powder  
dispersed in it.

25 While the slurry may be applied by  
spraying or brushing, the most convenient  
procedure for high volume commercial  
production of brazed assemblies is to dip  
the components into the slurry before or  
after assembly. This leads to deposition of  
the slurry on all the available surfaces of the  
components. Surface effects lead to  
preferential deposition between faying  
surfaces when assembled components are  
dipped. The particle size of the flux and  
metal powder should both be less than 200  
mesh (less than 75 microns) to ensure entry  
between the faying surfaces of assembled  
components.

30 By variation of the amount of water in the  
slurry and by control of other factors,  
particularly the rate of withdrawal of the  
component or assembly of components  
from the slurry, it is possible to deposit a  
slurry coating having a solids content of a  
few hundred gms/m<sup>2</sup> but an especially

useful range is 40—150 gms/m<sup>2</sup>. Such  
coating after the necessary drying step has  
sufficient adhesion to the aluminium  
component to allow it to be handled. It is,  
of course, necessary to pretreat the surface  
to ensure that the surface has been  
adequately degreased to allow the slurry to  
wet the surface.

35 The thus deposited coatings of flux and  
brazing alloy powder may contain sufficient  
flux to permit the brazing to be carried out  
in the normal oxidising atmosphere of a  
brazing furnace. However, the quantity of  
flux required for such operation is so high  
that large quantities of unsightly flux  
residue result and furthermore the costs of  
the brazing operation are significantly  
increased. Therefore, as a further feature of  
the invention the brazing operation is  
performed in a furnace having an  
atmosphere of a dry inert gas. The  
atmosphere is commonly dry oxygen-free  
nitrogen, i.e. dried to a moisture content of  
less than 250 p.p.m. water vapour and  
having a free oxygen content of less than  
3000 p.p.m. Other gases, which are inert to  
aluminium, such as cracked ammonia, may  
be employed provided that their free  
oxygen and moisture content are held down  
to the same levels. The furnace atmosphere  
is held at a temperature above the melting  
point of the powdered aluminium brazing  
alloy and of the flux, but below that of the  
aluminium or aluminium alloy components,  
which are to be joined by the brazing  
operation. This brazing procedure is  
satisfactory for almost all aluminium alloys  
which have a solidus temperature above the  
liquidus temperature of the brazing alloy.  
However, the flux provides less satisfactory  
results when the components to be joined  
(or one of them) has a Mg content in excess  
of 1%.

40 As already explained, the flux/brazing  
alloy ratio of the slurry may be varied  
through quite wide limits. It is, however,  
usually satisfactory to operate the process  
with a flux content of 5—15 gm/m<sup>2</sup> in the  
dried film. Thus the ratio of powdered  
brazing alloy filler metal and water to flux  
will preferably be arranged so as to deposit  
a desired coating weight of brazing alloy in  
conjunction with a flux content in the  
stated range. There is no upper limit for the  
amount of flux from the point of view of  
forming an effecting joint. However, the  
appearance of the work is marred by heavy  
fused flux residues and therefore it is  
preferred to restrict the flux to not more  
than 50 gms/m<sup>2</sup>.

45 The powdered brazing alloy/flux slurry  
may incorporate suspension agents and  
corrosion inhibitors, but these do not  
appear to be necessary in any operation  
where the dwell time of the slurry in the

bath is of limited duration. Small quantities of surface active agents may be included to assist in penetration of the slurry between the faying surfaces of an assembly.

5 The present process finds exceptional utility in the production of heat exchanger assemblies, such as oil coolers for motor vehicles.

10 As already stated, the flux consists essentially of a mixture of potassium fluoaluminates, essentially free of unreacted potassium fluoride. As herein used, "potassium fluoaluminate" refers to substances of the type formed by fusion of  $\text{AlF}_3$  and  $\text{KF}$ , such complexes having the formulae  $\text{K}_2\text{AlF}_6$  and  $\text{KAlF}_4$ . X-ray diffraction examination of the solidified residue of the fused eutectic mixture of  $\text{KF}$  and  $\text{AlF}_3$ , which occurs at about 45.8%  $\text{KF}$  and 54.2%  $\text{AlF}_3$ , indicates that virtually all the fluoride contents are in the form of  $\text{K}_2\text{AlF}_6$  and  $\text{KAlF}_4$ , which are very sparingly soluble in water and are non-hygroscopic. The fused eutectic consists of these two phases and is virtually free of  $\text{KF}$  and  $\text{AlF}_3$ .

25 The liquidus point of a mixture of potassium fluoaluminates varies depending upon the composition of the mixture, expressed as relative proportions of  $\text{AlF}_3$  and  $\text{KF}$ , reaching a minimum (about 560°C) at the aforementioned eutectic composition and it is accordingly preferred to employ a flux which complies closely with the eutectic composition. However, other flux compositions within the broader composition limits stated in our Patent No. 1,438,955 are also suitable in the process of the present invention. While the flux melting point shown in the published diagram (Journal American Ceramic Society, 49, pages 631-34, December 1966) rises very rapidly if the quantity of  $\text{KF}$  rises above that required for the eutectic, there is only a slight rise in melting point to about 574°C where the  $\text{AlF}_3$  rises above the eutectic up to a total of about 60% (50 mole %  $\text{AlF}_3$ ). For aluminium brazing operations, it is commonly preferred that the  $\text{AlF}_3/\text{KF}$  ratio of the potassium fluoaluminate be such that the flux becomes reactive at not more than 600°C. Preferably, the flux is an intimate mixture of  $\text{K}_2\text{AlF}_6$  and  $\text{KAlF}_4$  corresponding to an  $\text{AlF}_3/\text{KF}$  ratio between 60:40 and 50:50, in parts by weight, essentially free of unreacted  $\text{KF}$ .

55 At compositions corresponding to an  $\text{AlF}_3$  content below 60%, the mixture of potassium fluoaluminate complexes, in the dry state, consists essentially of  $\text{K}_2\text{AlF}_6$  and  $\text{KAlF}_4$ . At higher levels of  $\text{AlF}_3$  content within the stated range, the mixtures are constituted of  $\text{KAlF}_4$  with some unreacted  $\text{AlF}_3$  (which is insoluble in water) but,

again, essentially free of unreacted  $\text{KF}$ . Minor amounts of other fluorides (e.g.  $\text{LiF}$ ,  $\text{NaF}$  or  $\text{CaF}_2$ ) may be incorporated in the flux.

70 Because the potassium fluoaluminate flux does not deleteriously attack brazing alloy powder when mixed in water, the powdered flux-alloy bath has a useful life of several days or longer, whereas the use of a conventional chloride flux in such a bath would have a short life owing to attack on the brazing alloy by the chlorides. Indeed, it is found that a slurry in accordance with the present invention can be rejuvenated by a 10% weight addition of the flux and brazing alloy powder in the desired proportions.

75 Various additions may be made to the aqueous slurry of flux and brazing alloy powders without departing from the present invention. For example, conventional surfactants, thickeners and/or dispersing agents may be employed. In practice, however, satisfactory results have been achieved without any of these additives.

#### EXAMPLE I

One hundred parts by weight of -200 mesh size Al-12% Si brazing alloy powder and 25 parts by weight of -200 mesh size potassium fluoaluminate powder (a mixture of  $\text{KAlF}_4$  and  $\text{K}_2\text{AlF}_6$ ) were mixed with 75 parts by weight of deionized water and maintained in suspension in the resulting slurry by mechanical stirring. (Mesh Numbers are U.S. Sieve Series). Small specimens of cleaned aluminium, 2.5 cm x 2.5 cm, were dipped in the mechanically stirred slurry and withdrawn at a rate such that a uniform deposit of flux and metal powder remained on the surfaces of the specimens. After drying, the coating of flux and brazing alloy powder was removed from all but one surface of each specimen. Coating weights ranging from 30 to 180 grams per square metre were produced in this way, merely by varying the consistency of the slurry by dilution with water. Each specimen was successfully brazed to uncoated specimen in a tube furnace having an atmosphere of dry nitrogen.

#### EXAMPLE II

120 A slurry was prepared consisting of 4 grams of the potassium fluoaluminate flux powder, 160 grams of the Al-Si brazing alloy powder, and 108 ml of de-ionized water. This slurry was applied to surfaces of aluminium samples so as to achieve a coating weight (after drying) of 135 grams per square meter. Fully effective brazing was achieved with the samples thus coated, although the metal/flux ratio in this instance was 40:1.

## EXAMPLE III

5 A slurry consisting of 10 parts Al-10% Si  
brazing alloy powder and 1 part of flux (the  
eutectic mixture of  $KAlF_4$  and  $K_2AlF_6$ ) was  
mixed with sufficient water to provide, after  
immersion of plates of aluminium alloy  
designated AA3003 intended to form an oil  
cooler heat exchanger, in the air agitated  
slurry, dry coating weights ranging from 45  
to 135 g/sq. metre. The plates were racked  
while still wet. Uncoated end plates were  
used; the brazing alloy of the slurry on the  
exterior heat exchange plates provided the  
filler metal for brazing the end plates. After  
assembly, the unit was dried at 200°C for 5  
minutes, then placed in a furnace filled with  
dry nitrogen. The unit was heated to a  
temperature of 590°C over a 12-minute  
period and allowed to cool to 550°C before  
removal from the furnace. After cooling to  
room temperature, the parts were pressure  
tested using compressed air at 20 psig. No  
leaks were detected with those units with a  
solids coating weight of 70 g/sq. metre or  
more.

## WHAT WE CLAIM IS:—

1. A method of joining aluminium  
components by means of an aluminium  
brazing alloy having a melting point lower  
than that of the aluminium components, in  
which the assembled components are  
heated to a temperature above the melting  
point of the brazing alloy and below the  
melting point of said components in the  
presence of a potassium fluoaluminate flux,  
which is essentially free of unreacted  $KF$

characterised in that the flux and the  
brazing alloy are applied to the surface of at  
least one of the components as an aqueous  
slurry of finely divided flux and metal  
power, the film of slurry is then dried and  
the components are brazed by heating in a  
dry, oxygen-free inert gas atmosphere, the  
application of flux/brazing alloy slurry  
being controlled to apply 30—180 gms/m<sup>2</sup>  
of solids and the flux: brazing alloy ratio  
being selected to deposit at least 3.29  
gms/m<sup>2</sup> of flux.

2. A method according to claim 1 further  
characterised in that the ratio of brazing  
alloy powder to flux in said slurry is in the  
range of 4-40:1.

3. A method according to claim 1 or 2  
further characterised in that the brazing  
alloy/flux mix is deposited by immersing  
said one component into a bath of said  
slurry.

4. A method according to claim 1 or 2  
further characterised in that the assembled  
components are dipped into a bath of said  
slurry to deposit the brazing alloy/flux mix  
between the facing surface of said  
assembled components.

5. A method according to any of claims 1  
to 4 further characterised in that the inert  
gas is nitrogen.

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